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Metal-to-insulator transition in thin-film polymeric AC₆₀

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Metal-to-insulator transition in thin-film polymeric AC_{60}

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Abstract. We present an electron spectroscopy study of phase-pure AC_{60} thin films ($A = \text{Rb}, \text{Cs}$) in their monomer (face-centred cubic (fcc)) and polymer phases. A surface electronic reconstruction is observed in polymeric RbC_{60} , analogous to that reported for the fcc phase. As for pristine C_{60} , the occupied electronic states of AC_{60} fullerides are not dramatically affected by polymerization. The energy separation between the leading feature in photoemission and inverse photoemission is similar in both stable AC_{60} phases.

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These observations suggest that electron correlation effects are similar in the two phases, and that their different electronic behaviour is mainly related to the reduction of degeneracy of the polymer frontier states. Photoemission and electron-energy loss spectroscopy data show that the thin-film form of the RbC_{60} polymer is metallic at room temperature, and that it undergoes a metal–insulator transition at around 100 K. This transition temperature is much higher than that reported for the corresponding bulk phase and signals a poorer screening of Coulomb interactions at the film surface.

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1. Introduction

C_{60} polymers are fascinating solid state systems characterized by the presence of covalent intermolecular bonds arranged in a periodic pattern. Polymerization in C_{60} crystals may occur under various conditions such as exposure to intense laser light [1], irradiation by electrons [2] or ions [3], plasma discharge [4], high-pressure and high-temperature treatments [5, 6], or transfer of electrons to the fullerene species as in the alkali-intercalated compounds [7]. Depending on the phase, the bridge between two neighbouring molecules may consist of one or two covalent bonds [1], [8]–[11]; each C_{60} molecule may be linked to two, four, six or more molecules, allowing various network types in one [7], [11]–[13], two [14]–[16] and even three [17]–[20] dimensions.

The most commonly observed cross-linking mechanism is the so-called [2 + 2] cycloaddition, in which two adjacent double bonds reorganize into intermolecular single bonds generating a four-membered ring connecting two C_{60} molecules (polymerization via one single bond is much rarer, and only observed in alkali fullerides [11]). This type of bonding is present in the orthorhombic C_{60} polymer phase, where each molecule is connected to two neighbours to form parallel one-dimensional (1D)-polymer chains. A similar structure is observed in AC_{60} alkali fullerides ($A = \text{K, Rb, Cs}$) [7, 12, 13], where it is the thermodynamically stable structure at room temperature (RT) and below, whereas above 400 K these compounds exhibit a face-centred cubic (fcc) phase of rapidly spinning C_{60} monomers [21]. The symmetry of the AC_{60} polymer phase may be either orthorhombic or monoclinic depending on the intercalant. The 1D-polymer phase of KC_{60} is orthorhombic (Pmnn space group) [12, 22, 23], whereas the RbC_{60} and CsC_{60} polymer phases are monoclinic (I2/m space group) [22]–[24].

In contrast to the polymer phases obtained from neutral C_{60} , which are insulating like the pristine material, the 1D-polymer alkali fullerides display interesting electronic properties. Bulk studies on polymeric RbC_{60} (CsC_{60}) report a weakly metallic behaviour at RT [7, 12, 13] but

around 50 K (40 K) a metal-to-insulator transition occurs [25, 26] which yields a magnetically ordered phase with characteristic features of a spin density wave [7]. Although polymeric KC_{60} was initially reported to be metallic in the whole temperature range in which it is stable [25], conductivity studies [27]–[29] have shown a resistive upturn at 50 K which can be suppressed by applying hydrostatic pressure. The same study found that polymeric RbC_{60} is strongly insulating at low temperatures in the absence of applied pressure and that a transition from an insulating to a metallic state can be induced under pressure [28]. The existence of a metal–insulator transition in polymeric KC_{60} has been confirmed by a recent ESR and x-ray diffraction study [30]. Strong electron correlation has been claimed to be at the origin of these transitions from metal to magnetic insulators [7, 12, 13], in analogy to monomeric alkali fullerenes, which are generally characterized by a large on-ball Coulomb repulsion [31]. Although the existence of magnetic order at low temperature is indeed indicative of exchange interactions (hence of electronic correlation), the formation of covalent intermolecular bonds can have a large impact upon correlation effects, since in addition to introducing a finite electron density in the intermolecular regions polymerization leads to a modification in shape and effective degeneracy of the molecular orbitals.

Theoretical investigations [32]–[35] on polymerized C_{60} have shown that, except for the region near 8–9 eV below the Fermi level which contains the contribution of the σ orbitals corresponding to the covalent intermolecular bonds [32], the occurrence of [2 + 2] cycloaddition bonds does not lead to a dramatic modification of the electronic density of states (DOS) with respect to monomeric C_{60} . This has been confirmed by photoemission spectroscopy (PES) studies of the orthorhombic C_{60} polymer phase [36, 37] as well as x-ray emission spectroscopy characterizations of the 2D-polymer phases [16, 38]. In both cases, a significant broadening is observed, indicative of a reduction of orbital degeneracy.

The situation for alkali fullerenes is more complicated. The valence-band (VB) PES spectrum of polymeric AC_{60} fullerenes disagrees strongly with the expectation for the DOS of the neutral polymer chain [32], and the spectrum of the high-temperature monomer phase of the same compounds appears anomalously broad. The spectral lineshape of the polymer phase is more structured than that of the fcc phase, although the frontier feature appears at nearly the same binding energy and is separated by roughly the same energy from the most intense higher binding energy features in both phases [39, 40]. Due to such difficulties in the interpretation of the spectra, the impact of electron correlation and of polymerization on the electronic structure of these alkali fullerenes has been hard to assess experimentally. Also on the theory side, the task of determining the interplay of electron correlation with other interactions in a partially filled band derived from a degenerate molecular orbital remains challenging.

We have shown in a previous study [41] that the anomalous width of the PES features of the fcc phase is due to the occurrence of a charge reconstruction of the surface layer of the film, which is C_{60} -terminated (see [41] and references therein). We show here that a similar phenomenon occurs in the polymer phase of RbC_{60} , and that it results in the coexistence of neutral C_{60} monomers and charged C_{60} polymer chains at the film surface. The orientation of the polymer chains with respect to the surface layer is discussed. We find evidence for a metal–insulator transition in the thin film at a much higher temperature than that reported for the bulk material. The higher transition temperature is arguably related to the occurrence of the charge reconstruction and to poorer screening of Coulomb interactions at the surface. We establish that also in alkali fullerenes polymerization via [2 + 2] cycloaddition does not strongly modify the occupied DOS, and provide evidence that correlation effects are similar in both

stable phases of AC_{60} . These similarities suggest that the difference in electronic behaviour between the two phases originates only from the reduced degeneracy of the frontier polymer states [32].

2. Experimental details

A phase-pure RbC_{60} thin film was prepared on an Ag(100) single crystal by intercalating a C_{60} film with an understoichiometric amount of Rb, followed by ‘vacuum distillation’ at 525 K to yield the fcc phase [42]. High-resolution photoemission spectra of the RbC_{60} film in both thermodynamically stable phases were acquired at the SuperESCA beamline [43] (base pressure $< 5 \times 10^{-11}$ mbar) of the ELETTRA synchrotron radiation facility. The sample was mounted on an He-cooled manipulator and could be heated with a filament placed behind it. Phase purity was established by photoemission (see below). Photoelectrons were collected at normal emission and the binding energy was calibrated by recording the Fermi edge of the clean Ag substrate. Core-level spectra (Rb 3d and C 1s) were measured at a photon energy of 400 eV with a resolution of 0.15 eV, while for the VB spectra the photon energy was 129 eV and the resolution 0.036 eV. For these photon energies the kinetic energy of the emitted photoelectrons is large enough that band structure effects in the final state can be neglected. The photon energies for the core level and VB spectra were chosen so that the photoelectron kinetic energy and hence the electronic mean free path are roughly the same for VB and C 1s electrons.

The RbC_{60} polymer phase was obtained letting the film cool down slowly from the fcc phase to RT. The same growth procedure was repeated at the Zernike Institute for Advanced Materials in an ultra-high vacuum chamber devoted to electron energy loss spectroscopy, which is also equipped with low-energy electron diffraction (LEED). High-resolution electron energy-loss (HREEL) spectra were acquired *in situ* on the polymer phase using a commercial DELTA 0.5 spectrometer (SPECS). The primary electron energy was 4 eV, and the resolution (defined by the full-width at half-maximum of the elastic peak) was better than 3 meV. The spectra were measured in specular reflection geometry at an incidence angle of 55° . CsC_{60} films were prepared by a similar procedure on an Au(110) substrate as detailed in [44]. The PES measurements on polymeric CsC_{60} were carried out with a standard He discharge lamp (using the He I resonance at 21.2 eV) and a hemispherical electron analyser with 5° acceptance angle (VG100AX). The Fermi-level position was determined from spectra recorded on the clean Au(110) substrate, and the emission due to the He II satellites was subtracted. All spectra were acquired at normal emission with a resolution of 0.15 eV. The IPES measurements were performed on both RbC_{60} and CsC_{60} prepared *in situ* at the IPES Trieste laboratory [45], with an energy resolution of 0.35 eV as measured on the Fermi edge of the clean substrate. The spectra were normalized at each point to the incident electron beam current. Experimental details of the instrumental setup can be found in [46]. The PES and IPES measurements on CsC_{60} were carried out at RT on films prepared under the same conditions and thoroughly characterized by Auger electron spectroscopy and LEED to ensure that the same phase was obtained. In all experiments, the temperature was monitored via a thermocouple inserted in a hole on the side of the substrate.

3. Charge reconstruction and frontier states in polymeric AC_{60}

We start our analysis from the high-resolution photoemission (PES) spectra acquired on RbC_{60} , shown in figure 1, which convey information about the charge state and chemical environment of

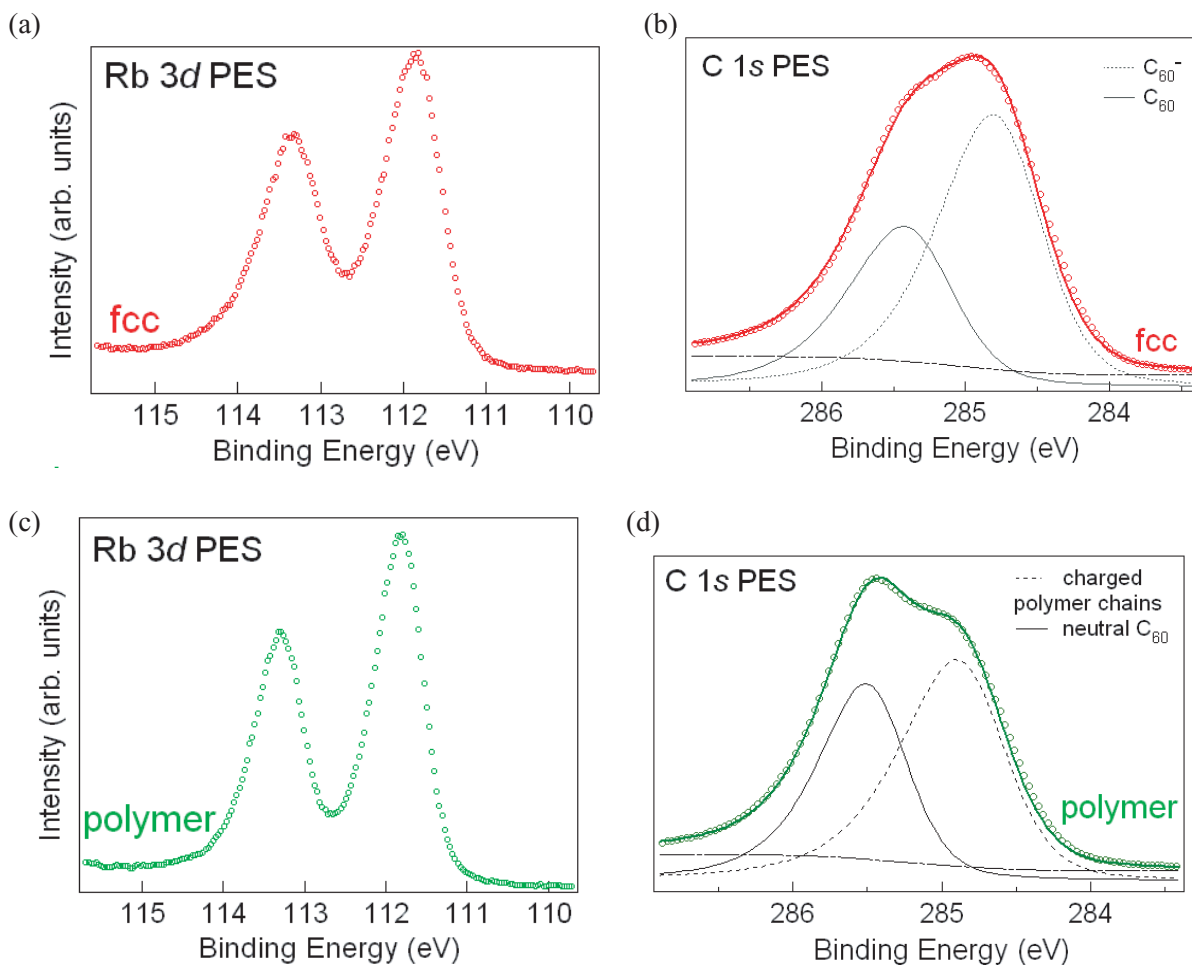


Figure 1. (a, c) Rb 3d photoemission spectra of the fcc (a) and polymer (c) phases of RbC₆₀; (b, d) C 1s photoemission spectra of the same two phases (the fcc spectra are taken from [41]). A fit of the latter spectra with two components is also shown reflecting the presence of two surface charge states (see text). All spectra were acquired with $h\nu = 400$ eV.

the Rb and C atoms in the film. The PES spectra acquired on the fcc phase are taken from [41]. The Rb 3d spectra of the fcc (figure 1(a)) and polymer phases (figure 1(c)) both consist of a single spin–orbit doublet with energy splitting of 1.5 eV and the expected intensity ratio (2 : 3) for the final state splitting between the 3d_{3/2} and 3d_{5/2} states. The presence of only one Rb doublet indicates that all Rb ions have a similar environment in both phases, i.e. they occupy the same type of interstitial site (octahedral in the fcc phase and pseudo-octahedral in the polymer phase), which proves the quality of our film.

The C 1s spectra of the two phases, shown in figures 1(b) and (d), are seen to contain (at least) two components, approximately 0.6 eV apart. We have previously shown [41] that the two spectral components in the fcc phase correspond to two distinct molecular charge states at the film surface, arising from a charge reconstruction brought about by the polar character of the C₆₀ termination. Such charge reconstruction entails a charge density of $-1/2 e$ per C₆₀

molecule in the surface layer, which due to strong electron localization on single molecules [7, 21] corresponds to a situation in which half the molecules are neutral and half carry a 1– charge (at least on the subfemtosecond time scale of the PES process). The two components in the C 1s spectrum of the fcc phase thus reflect the presence of 50% neutral and 50% charged fullerene molecules in the surface plane, whereas the subsurface molecular layers consist entirely of charged molecules. The observation of two distinct C 1s components in the polymer phase is similarly indicative of the presence of different charge states at the surface of the polymerized RbC₆₀ film. In both phases the component corresponding to the neutral species appears at higher binding energy due to inter-electron repulsion [41], with the lower binding energy component originating from charged species. This assignment is consistent with the relative intensity of the two components and with their dependence upon the emission angle of the photoelectrons in both phases, as shown for the fcc phase in [41].

The C 1s spectra of the fcc and polymer phases were fitted with Voigt-like functions (see [41] for the details of the fitting procedure). The width of each component reflects the modulation of Madelung potential at different C sites, the experimental resolution and the electron–phonon broadening. Although in fcc phase the two C₆₀ components were taken to be of same width (0.85 eV), in the polymer phase the charged component at lower binding energy is found to be broader than the neutral one. In fact, the width of the neutral component is defined by the shape of the spectral maximum around 285.5 eV binding energy, whereas the lineshape appears rather broad at lower binding energy (figure 1(d)), so that two different widths have to be used for the neutral and charged components. This can be rationalized if the neutral component consists of C₆₀ monomers as in the fcc and dimer phases [41], since the molecular distortion induced by the formation of the intermolecular bonds in a polymer chain results in a larger variety of chemical environments. Indeed, also in a two-component fit of the C 1s spectrum of the metastable dimer phase of RbC₆₀ (see [41]) allowing for different widths the charged component is found to be wider than the neutral one, and the width ratio is larger in the polymer than in the dimer phase, which is consistent with the more severe distortion of the fullerene cages in [2 + 2] cycloaddition polymerization with respect to the single-bond dimerization. It is not surprising that the neutral species in the polymer phase of RbC₆₀ do not form neutral polymer chains, since, as mentioned in the introduction, neutral C₆₀ does not spontaneously polymerize at RT under our experimental conditions. Moreover, our suggested surface morphology is incompatible with the formation of neutral chains at the surface (see section 4).

In all three phases, the charged component contains a contribution from surface molecules as well as from subsurface (bulk) ones. Our fit of the polymer spectrum in figure 1(d) gives a bulk- to total-signal ratio of 13.5%, which is close to that found (15%) for the dimer phase and slightly lower than the one (25%) for the fcc phase [41]. These low values are consistent with the relatively low inelastic mean free path typical of fullerenes [47]. The lower mean free path in phases containing intermolecular bonds suggests that the presence of intermolecular electronic clouds results in an increased electron scattering rate. Also, the surface morphology (see section 4) might affect the experimental relative weight of the components.

Figure 2 shows the VB photoemission (PES) and inverse photoemission (IPES) spectra of fcc RbC₆₀ (a) together with the analogous spectra of polymeric RbC₆₀ (b) and CsC₆₀ (c). The position and shape of the features in the three PES spectra are in agreement with the previous studies [39, 40]. As demonstrated in [41], the PES spectrum of the fcc phase of RbC₆₀ can be modelled as the sum of two C₆₀ VB lineshapes rigidly shifted with respect to one another,

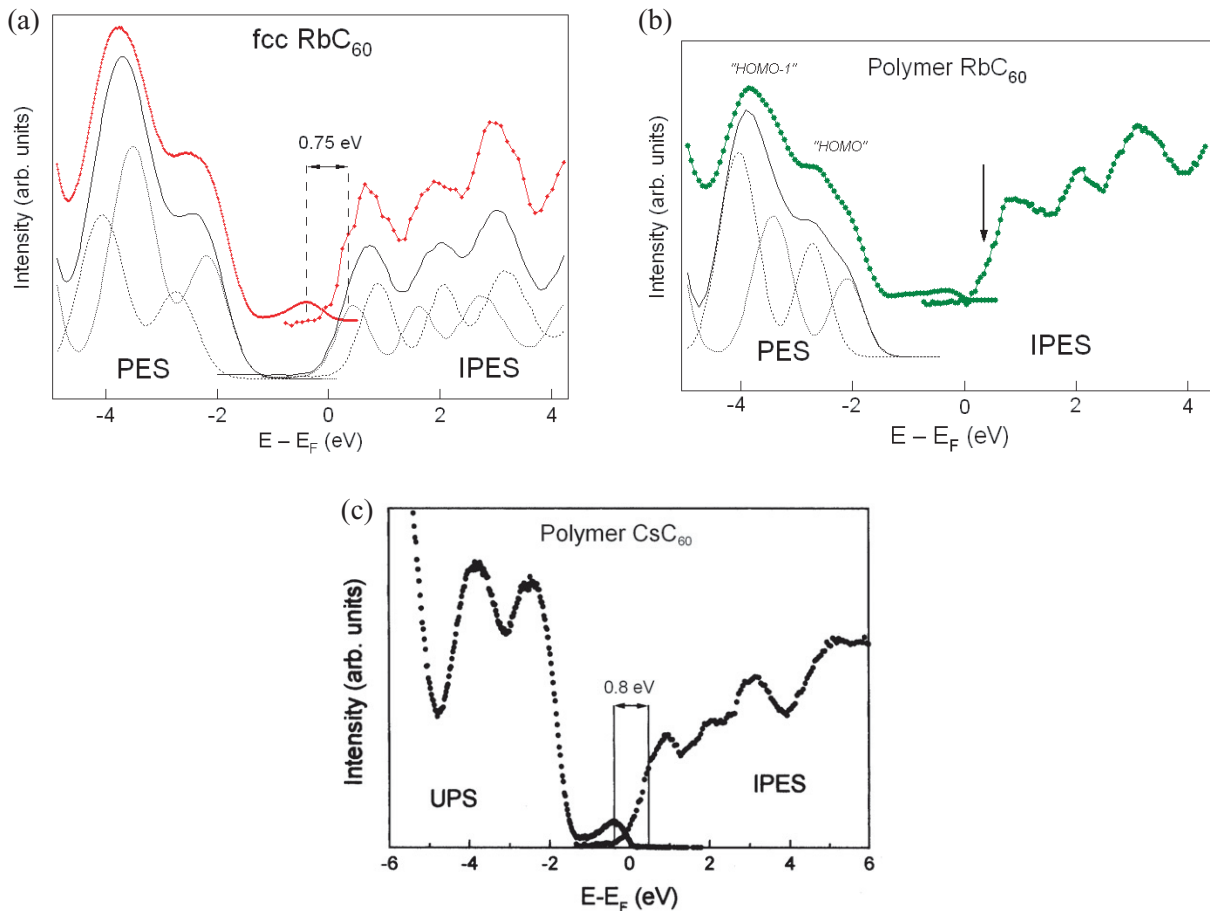


Figure 2. (a) Photoemission ($h\nu = 129$ eV, from [41]) and inverse photoemission spectra of fcc RbC₆₀. A model of both in terms of two components is presented, corresponding to two surface charge states. (b) Photoemission ($h\nu = 129$ eV) and inverse photoemission spectra of the RbC₆₀ polymer phase. The photoemission spectrum of polymeric RbC₆₀ (excluding the frontier feature) is reproduced as the sum of two C₆₀ VB photoemission lineshapes, corresponding to two surface charge states (see text). (c) UV-photoemission ($h\nu = 21.2$ eV) and inverse photoemission spectra of polymeric CsC₆₀.

corresponding to neutral and charged monomers, with approximately the same relative intensity and energy separation observed in the C 1s core level. The model is reproduced on the left-hand side of figure 2(a) (the frontier PES feature, corresponding to the occupied portion of the states derived from the lowest unoccupied molecular orbital—LUMO—of the fullerene molecule, is obviously not included in the model).

The IPES lineshape of fcc RbC₆₀ resembles the one acquired with the same experimental setup on pristine C₆₀ (own data, see figure 2(a)), but the width of the spectral features is much larger, similar to the PES case. The frontier peak in IPES, which corresponds to the unoccupied portion of the LUMO-derived states, appears structured with a shoulder towards the Fermi level. Just like for the C 1s and VB PES spectra of the same phase, two charge states contribute to the IPES spectrum of fcc RbC₆₀. On the right-hand side of figure 2(a) we present a model of this spectrum as the superposition of two C₆₀ IPES lineshapes rigidly shifted with respect to

one another by 0.45 eV, close to the binding energy difference observed between the molecular charge states in the VB PES spectrum of the same phase (0.5 eV). The IPES component arising from the charged monomers might, in principle, be broader or more structured than the neutral one, due to the existence of distinct possible IPES final states corresponding to the different total-spin configurations of the two LUMO electrons. Nonetheless, our model with two C_{60} lineshapes provides a good fit of the IPES spectrum of fcc RbC_{60} , as visible in figure 2(a).

As mentioned in the introduction, the VB PES spectrum of polymeric RbC_{60} (figure 2(b)) is much more structured than the theoretical DOS for the polymer chain [32] or the photoemission spectrum of the orthorhombic C_{60} polymer [36, 37]. We see here that such discrepancy results from the presence of two different species at the surface of the polymerized film, namely charged polymer chains and neutral monomers. The PES spectrum of the RbC_{60} polymer can be well reproduced as the sum of two C_{60} lineshapes, as shown in figure 2(b) for the spectral region corresponding to features derived from the highest occupied molecular orbital (HOMO) and HOMO-1 orbital of C_{60} . Just as for the fcc phase, the model does not include the frontier PES feature of the polymer phase, which is further discussed in section 5. It is remarkable that the frontier states have a very similar lineshape in both fcc and polymeric RbC_{60} . This similarity and the good agreement obtained with our model in terms of the PES profile of pristine C_{60} , demonstrate that in alkali fullerides the occupied electronic DOS is not dramatically altered by the occurrence of polymerization, as previously found for the undoped fullerite case [36, 37].

In the IPES spectrum of polymeric RbC_{60} (acquired at 170 K) the leading feature is rather broad and presents a weak shoulder towards E_F (see arrow in figure 2(b)) in the energy region where the shoulder to the LUMO-derived peak is observed in fcc RbC_{60} . The energy position of the shoulder cannot be precisely estimated due to the relatively low signal-to-noise ratio, but a similar, better resolved shoulder can be observed in the IPES spectrum of the polymeric phase of the sister compound CsC_{60} (figure 2(c)). Contrary to cubic monomer phases where the LUMO-derived band supposedly retains its three-fold degeneracy, the partially occupied frontier orbital in the polymer phase is non-degenerate [32, 34, 48], leading to a more complex unoccupied DOS. At the same time, two surface charge states are present (possibly also in CsC_{60}). Due to such complexity, we do not attempt to give a full model for the IPES spectra of the polymer phases. Interesting information may still be extracted from the details of the frontier features in both PES and IPES spectra, which arise from the half-occupied non-degenerate frontier polymer orbital. Performing a two-component fit of such features we find that the shortest PES–IPES separation in polymeric CsC_{60} is very close to that observed in fcc RbC_{60} (~ 0.8 eV, see panels (a) and (c) of figure 2). This energy separation is also consistent with the spectra of polymeric RbC_{60} , as expected since the congruence of the phase diagram of the two compounds [49] indicates that they have virtually identical electronic structures.

In all three phases, the PES–IPES energy separation corresponds to the splitting of the occupied and unoccupied portion of the LUMO-derived state(s) into a lower and upper Hubbard sub-band due to correlation effects. The similar energy separation observed in monomer and 1D-polymer phases indicates that the effect of correlation is similar in both types of systems. This is in agreement with our result that the occupied electronic DOS near E_F is not fundamentally modified by the formation of covalent intermolecular bonds, and further suggests that the electrons in the outermost valence clouds of the polymer chains are mostly localized on single molecular units, as in the case of monomer phases [7, 21, 50], resulting in a similar electronic screening.

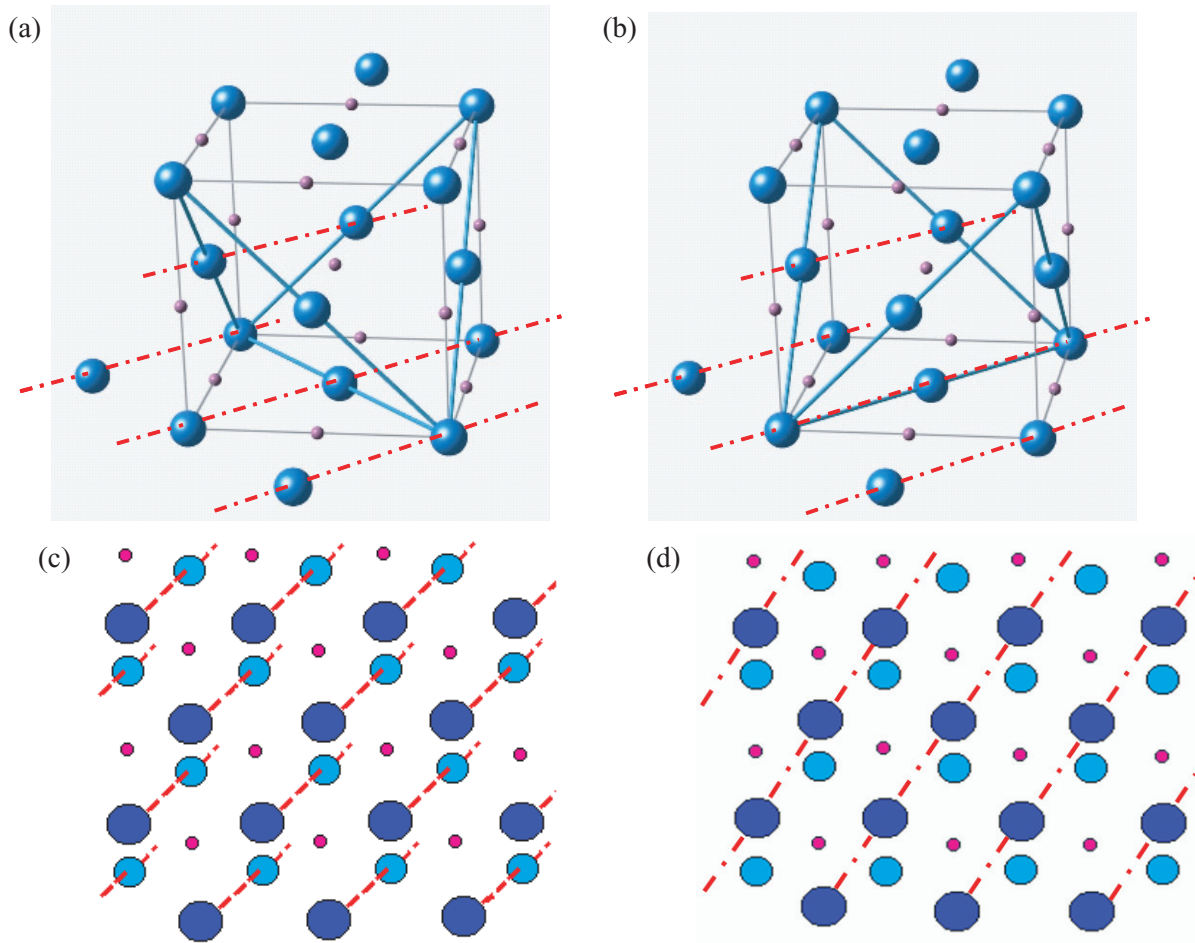


Figure 3. Comparison between the bulk (upper panels) and surface (lower panels) structures of the fcc and polymer phases. In (a) and (b), the large circles (blue) represent the C₆₀ molecules and the smaller (purple) ones correspond to the positions of the Rb ions (for clarity the relative sizes and distances are not reproduced). The four equivalent planes of triangular symmetry in the conventional fcc unit cell are drawn as triangles (bold blue lines). The dashed red lines indicate the directions of the polymer chains. The two choices shown in (a) are perfectly equivalent, with the polymer chains tilted with respect to the surface layer as shown in (c). The two choices in (b) are also equivalent and result in the same pattern of in-plane surface polymer chains, shown in (d) only for the surface layer. In (c) and (d), the large and medium blue circles represent the C₆₀ molecules of the first and second layers, respectively, whereas the smaller purple circles represent Rb atoms.

4. Surface structure of the polymerized film

As shown in previous studies [39, 41] the fcc phase of AC₆₀ is characterized by a faint (1 × 1) hexagonal LEED pattern, which indicates that the monomer film termination is a (1 1 1) plane as in thin films of pristine fullerite. In figure 3, we consider the possible film terminations in

the polymer phase. The bulk lattice structure can be described as consisting of polymer chains parallel to the (1 1 0) direction of the monomer (fcc) lattice, as indicated by the dashed lines in the upper panels of figure 3. The actual direction of polymerization with respect to the hexagonal termination plane of the film is however not uniquely determined. In the polymerized film the intermolecular bonds can either be parallel to the termination plane or tilted at an angle of approximately 54.7° with respect to it, in which case the covalent polymer bonds connect molecules of the surface layer with subsurface ones.

The two cases are depicted in panels (a) and (b) of figure 3. Fixing the orientation of the polymers with respect to the axes of the conventional cubic cell, four possible choices are given for the hexagonal (1 1 1) termination plane, drawn as bold triangles. These four possible choices correspond to the four diagonal planes of the cube representing the fcc cell, namely the (1 1 1) and (1 -1 -1) planes (figure 3(a)) and the (-1 1 1) and (1 -1 1) planes (figure 3(b)). The first two choices are equivalent, and correspond to the case where the polymer chains are tilted with respect to the surface plane. A scheme representing the top-view of the surface and subsurface layers in this case is shown in figure 3(c). The second two correspond to the situation with in-plane polymer chains (figure 3(d)).

If the surface termination of the film was simply the truncation of the polymer lattice, the surface pattern for both the in-plane and out-of-plane cases would readily be identified from figures 3(c) and (d). The LEED pattern of the polymerized film should thus reveal, in principle, which termination is preferred. In particular, in-plane polymerization leads to a characteristic pattern which is the superposition of three oblique (quasi-hexagonal) domains as observed in another polymeric fulleride, Li_4C_{60} [51]. The LEED pattern of polymeric RbC_{60} did not show any deviation from the hexagonal 1×1 pattern of the fcc phase, suggesting that the polymer chains are tilted with respect to the surface plane. In this geometry, the neutral surface species that are present due to the surface charge reconstruction cannot form neutral polymer chains, as these would run in the surface plane in a direction that is completely different from that of the charged chains. The proposed surface morphology is therefore consistent with our PES data (see discussion in section 3). It should be stressed, however, that the presence at the film termination of both neutral monomers and charged cages linked by intermolecular bonds may lead to a complex surface morphology. Our LEED study is not conclusive, since an average hexagonal pattern could perhaps arise also if the polymer chains lie in the surface plane but distributed in a disordered fashion, similar to that observed in photopolymerized C_{60} where strains in the film induce a disordered surface without long-range order or herringbone-like structures [52]. We cannot also *a priori* exclude the occurrence of a minority population of charged monomers at the surface of the polymer phase, similar to what is observed in the metastable dimer phase (see [41, 50] and references therein). A microscopy study is best suited to settle this issue.

5. Polymer metal-to-insulator transition at the surface

As mentioned in section 3, the feature closest to E_F in the PES spectrum of polymeric AC_{60} (shown in more detail in figure 4(a)) arises from the non-degenerate frontier orbital of the charged polymer chain. This spectrum displays a maximum between 0.35 and 0.4 eV binding energy followed by a linear intensity decrease towards the HOMO-derived states, as observed previously [39]–[41]. The photoemission intensity drops slowly towards the Fermi level where a nonzero signal is detected suggesting that the thin-film form of polymeric RbC_{60} is metallic at RT. The intensity ratio between the frontier (LUMO-derived) states and the HOMO-derived

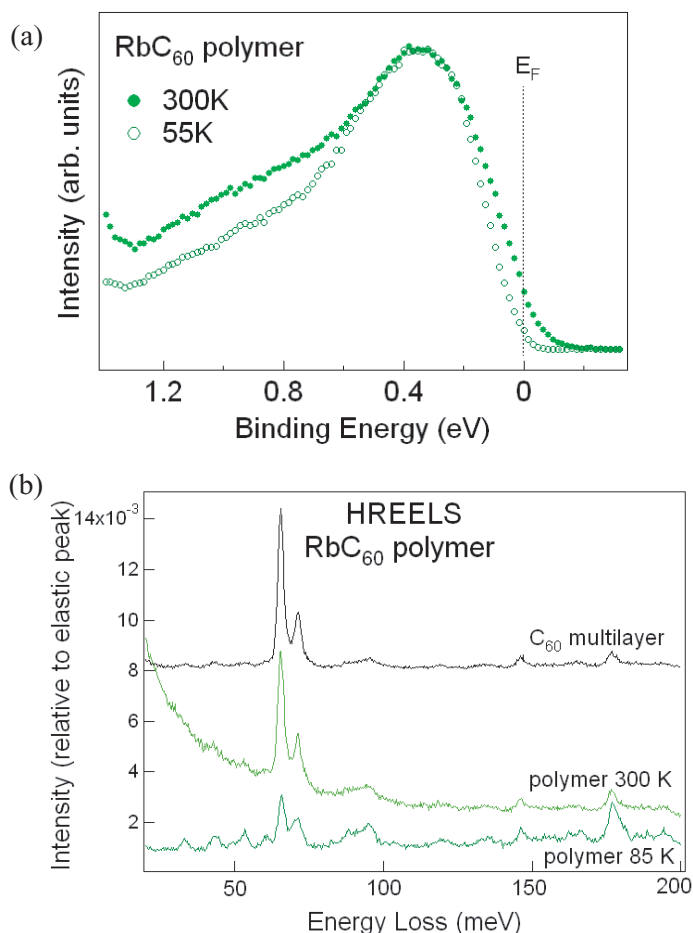


Figure 4. (a) Photoemission ($h\nu = 129$ eV) spectrum of the frontier polymer states at RT and at 55 K. (b) HREEL vibrational spectra of the polymer phase at RT (green) and at 85 K, compared with the analogous spectrum of the pristine C₆₀ film at RT. Note the strongly asymmetric (metallic) background at low loss energy in the RT polymer spectrum.

states is virtually the same in the fcc and polymer phases of RbC₆₀, which demonstrates that also in the polymer phase the extra charge donated by the alkali intercalant appears in LUMO-like states, consistent with the fact that the formation of intermolecular bonds involves higher binding energy orbitals [32].

As visible in figure 4(a), the frontier polymer states display remarkable temperature dependence. At RT a finite spectral intensity is observed at and above E_F , with a tail at negative binding energy much wider than the Fermi–Dirac distribution at RT (even accounting for the experimental resolution). Such a non-Fermi-liquid profile at E_F is analogous to that of the LUMO-derived spectrum of the fcc phase and similarly stems from an electron–phonon coupling effect [41]. As the temperature is lowered, the spectral intensity at E_F decreases and a gap seems to open at the Fermi level. The vanishing spectral intensity in the spectrum acquired at 55 K suggests an insulating character of the polymerized film at this temperature. Given the important effect of electron–phonon coupling on the spectral features, it cannot be

unambiguously concluded from these data alone whether the temperature dependence in the lineshape is due to a transition from a metallic to an insulating state, or whether it originates from the lower spectral weight associated with electron–phonon satellites at low temperature.

It is impossible to reliably monitor analogous changes in the IPES spectrum of this phase, due to the poorer energy resolution. We have therefore performed high-resolution electron energy-loss (HREELS) experiments to further investigate the occurrence of a metal-to-insulator transition in the film. Figure 4(b) shows the HREEL spectra of polymeric RbC_{60} at RT and at 85 K. The spectrum of pristine C_{60} , also shown for comparison, presents somewhat weaker features at virtually the same energies of the modes observed in polymerized RbC_{60} . The similarity between the spectra is not surprising given the experimental resolution and the fact that the surface layer of the RbC_{60} film, which contributes heavily to the HREEL spectrum, consists for 50% of neutral monomers. The only visible difference concerns the most intense C_{60} mode at 65 meV, which in the low-temperature RbC_{60} spectrum is less intense and displays a slight shift of 0.5 meV to higher energy. The shift of this mode in the polymer spectrum as well as the more pronounced character of the other modes are probably related to polymerization, which leads to a ‘mixing’ of the various C_{60} modes, thus affecting their energy and width, and in general to an enhanced dipolar activity of the modes with respect to monomer phases.

In the RT HREEL spectrum a clear asymmetric background rises towards the position of the elastic peak, which we interpret as due to electronic excitations from states below to states above E_F , hence indicating that metallic behaviour is present at ambient temperature. The metallic-like asymmetry could be observed also in an HREEL spectrum acquired at 110 K (not shown). A very flat background can instead be seen at 85 K, which confirms the insulating nature of the polymer phase at low temperature.

The comparison between our PES and HREELS results shows that the decay of the intensity at E_F in the spectra of figure 4(a) is indeed the signature of the opening of a gap accompanying a metal–insulator transition in the polymerized film, which occurs between 90 and 110 K. This metal–insulator transition is the thin-film analogue of the transition reported in the bulk at 50 K, which has been associated with strong electron correlation effects possibly linked with a low-dimensional electronic structure [7]. The occurrence of phase transitions at fulleride surfaces is well documented, and differences in transition temperatures are reported in some cases [53]. A higher temperature for the metal–insulator transition may be expected at the film surface, as the truncation of the bulk structure and the lower coordination results in a poorer screening of Coulomb interactions, as well as in the presence of surface electric fields responsible for the occurrence of the charge reconstruction and which could affect the charge transport. Moreover, the different local coordination and lattice constant in the film can have an impact on the electronic structure, which is known to be strongly dependent on the molecular environment in fullerenes and at their surfaces [54]–[58].

While the polymer phase is insulating at low temperature, a (metastable) low-temperature monomer phase exists in AC_{60} compounds which is strongly metallic [50, 59]. As electron correlation is similar in monomer and polymer phases (section 3), the different metallic behaviour of the low-temperature polymer and monomer phases in the bulk is most probably due only to the lifting of degeneracy of the frontier states in the polymer phase [32, 34] and the corresponding narrowing and weak dispersion of the t_{1u} -derived band [48]. Our data and analysis are consistent with an electron-correlation mechanism for the metal-to-insulator transition in the polymer phase.

6. Summary

We have investigated phase-pure RbC_{60} and CsC_{60} thin films by means of photoemission, inverse photoemission and electron energy loss spectroscopy. The surface electronic reconstruction observed in fcc RbC_{60} is also found to occur in the polymer phase of the same compound. After discussing the possible film termination, we provide partial evidence that the intermolecular bonds are tilted with respect to the film surface. Our analysis of the VB photoemission lineshape of polymeric RbC_{60} demonstrates the strong similarity of the electronic structure of monomer and polymer AC_{60} phases. The similar energy separation between the leading spectral feature in polymer and fcc phases suggests that the magnitude of electron correlation is comparable in both systems and hence that their difference in electronic behaviour is related only to the reduction of the effective degeneracy of the frontier (LUMO-like) states in the polymeric system. The thin-film RbC_{60} polymer phase is metallic at RT but undergoes a metal–insulator transition at around 100 K, which is 50 K higher than the transition temperature reported for the corresponding bulk phase and signals a less effective screening of Coulomb interactions at the polymer surface.

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